

Appln. No. 10/806,749
Amdt. dated November 17, 2005
Reply to Office Action of August 30, 2005

REMARKS/ARGUMENTS

Claims 35 - 41, 43 - 46, 49, 50 and 57 - 61 are in the application for consideration. Reconsideration of the application is requested in view of the statements appearing below herein.

1. Applicants wish to bring to the attention of the United States Patent and Trademark Office two new references of which they have recently become aware. The references are:

1. Japanese Kokai Publication No. S59-1294 entitled "Multicolor Thermosensitive Recording Material".

2. Japanese Kokai Publication No. S59-194886 entitled "Two-Color Thermosensitive Recording Material".

Applicants have obtained English-language translations of these references. A copy of each of these references and a copy of each translation is enclosed for the convenience of the examiner. It is requested that these references be made of record in the application and considered by the examiner in the prosecution of the application.

2. New claims 57 - 61 have been added in the application. The subject matter of these claims is fully supported by the application as originally filed and does not include any objectionable new matter.

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Claims 57 is dependent upon amended claim 35 and is directed to the embodiment of applicants' invention wherein at least one of the image-forming layers includes a compound which forms color intramolecularly. This embodiment is described, for example, at page 19, lines 16 - 26, page 29, lines 15 - 20, and recited in original claim 16.

Claims 58 - 61 are directed to the embodiment of applicants' invention wherein the imaging member has an interlayer which includes a material which undergoes a phase change upon the application of heat. In essence, new claim 58 is directed to the embodiment recited in original claim 37 which has been indicated as reciting allowable subject matter. Claims 59 - 61 which are dependent from claim 58 are clearly supported for the same reasons discussed above.

4. In the Office Action the examiner has taken the following actions:

A. Claims 35 and 36 have been rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,686,159 ("Langan").

B. Claims 38 - 41, 46, 49 and 50 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Langan

C. Claims 42 - 45 have been allowed.

D. Claims 37, 47 and 48 have been objected to as being dependent upon a rejected base claim but indicated as containing allowable subject matter.

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5. The claims presently in the application are patentable over the references of record. Claim 35 has been amended by incorporating therein the subject matter of claim 42 (now canceled) which was indicated as being allowable. Claim 35 now recites a thermal imaging member which includes three image-forming layers and two interlayers.

Amended claim 35 is patentably distinguishable over Langan and over the newly-cited Japanese Kokai references. Langan discloses a piggyback label article which includes two labels, each having a substrate and an image-forming layer. There is no suggestion in Langan whatsoever relating to a thermal imaging member having three image-forming layers and two interlayers.

Amended claim 35 is also patentable over Japanese Patent Kokai S59-1294 ("Kokai 1294") and Japanese Patent Kokai S59-194886 ("Kokai 194886"). Kokai 1294 describes a multicolor thermosensitive recording material which includes an intermediate layer of water-soluble resin interposed between a first thermosensitive coloring layer and a second thermosensitive coloring layer. Each coloring layer includes a leuco dye and a developer. The reference states that "...a material with a high melting point can be used in the upper layer, and a material with a low melting point can be used in the lower layer...".

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Kokai 194886 describes a two-color thermosensitive recording method which utilizes a recording member having a high temperature recording layer positioned on a support above a low temperature recording layer. The high temperature recording layer is colored by heating it to a temperature and for a period of time that is insufficient for the low temperature recording layer to reach a temperature at which it would be substantially colored. The low temperature recording layer is heated to a temperature and for a time sufficient to color the layer although the high temperature recording layer is not substantially colored.

Kokai 1294 and Kokai 194886 nowhere teach or even remotely suggest a thermal imaging member having three image-forming layers and two interlayers such as that recited in amended claim 35 and the claims dependent thereon.

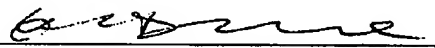
Reconsideration of the rejections based on Langan and withdrawal thereof are respectfully requested.

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6. New claims 58 -61 are also patentably distinguishable over Langan and over the newly-cited Japanese Kokai references. Claim 58 recites a thermal imaging member having first and second image-forming layers with an interlayer positioned between them. The interlayer includes a material which undergo a phase change upon the application of heat. Langan and the Japanese Kokai references do not teach or even remotely suggest a phase change interlayer in such a thermal imaging member.

In summary, the claims presently in the application have been shown to be wholly novel and patentable over the references of record. Reconsideration of the application and allowance of the claims are respectfully requested.

Respectfully submitted,


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Enclosures

⑨ 日本国特許庁 (JP)

⑩ 特許

⑫ 公開特許公報 (A)

昭59—

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6906—2H

⑬ 公開 昭和59年(1

発明の数 1
審査請求 未請求

⑭ 多色感熱記録材料

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明 細 書

1 発明の名称

多色感熱記録材料

2 特許請求の範囲

- (1) エイロ架料と顔色剤とを主成分とした第1の感熱発色層と第2の感熱発色層との間に、水溶性樹脂の中間層を介在させたことを特徴とする多色感熱記録材料。

3 発明の詳細な説明

本発明は多色感熱記録材料に関し、詳しくは異なつた加熱温度で異なつた色に発色する複数の感熱発色層を積層した多色感熱材料に関する。

させる顔色剤（発色助剤）とを含む層が鮮明であり、しかもカブリ現多く利用されている。

ところで、感熱記録材料は加熱に発色画像が得られるため図画、に用いられるばかりでなく、電子シミリ、テレンクスなどの各種機の出力記録等の分野で利用されて用途によつてはとくに必要なデータ明確に表示するため、その部色を他の部分の発色の色と変えとが望ましいことは当然である。

特記

感熱発色層では、従来のものは、上層に低温度で感熱発色する物質を含有させ、下層に高温度で感熱発色する材料を含有させているため、感熱発色材料の溶解温度に誤差があり、その材料は制約されるし、また多層塗工するに際し、上下層に水溶性樹脂を同じくするため、上層の塗布の時に下層の一部が溶解し、上層と混じり合い、地肌カブリを生じるという問題がある。さらに、上下層の間に非極性溶媒に可溶性のポリマーを含有する中間層を設けることも提案されているが、この中間層の上に水分散系の上層を形成する際、感熱発色層塗布液と中間層との濡れが悪いために、実質上均一な感熱発色層を形成することは困難であり、結果として不鮮明な多色画像しか与えない。

本発明の目的は、上記のごとき従来技術の問題点を解消して良質の多色画像が得られるようにした多色感熱記録材料を提供することにある。

即ち、本発明は、支持体上にロイコ染料とそれに対する顔色剤とを主成分とした複数の感熱発色層が積層された多色感熱記録材料において、第1

の感熱発色層と第2の感熱発色層樹脂の中間層を介在させたことを感熱記録材料を提供するものである。

本発明においては、特別の中間層により、上層（第2の感熱発色層の感熱発色層）の影響を受けず、なく、しかも中間層の上に上層を塗が良好である。その上、中間層を調節することにより、上層と上層温度を有する発色材料が適用で高速記録性を望みかつ初期の地肌時の地肌カブリの防止を強く望む。樹脂温度の高い材料を用い、下層低い材料を用いることができる。層の付増量は、一般的には0.5～好ましくは1～5 g/m²が適当で、

本発明では、上層と下層の感熱水溶性樹脂の中間層を設けたもの場合、水溶性樹脂としては、例えばアルコール、メトキシセルロース、

ルコース、カルボキシメチルセルロース、カルボキシエチルセルロース、ポリビニルピロリドン、ポリアクリルアミド、ポリアクリル酸、澱粉、ゼラチンなどが挙げられる。なお、これら水溶性樹脂との併用で、例えばステレン-ブタジエン共重合体、塩化ビニル-酢酸ビニル共重合体、ポリ酢酸ビニル、ポリアクリル酸エステル、ポリブタジエンメタクリレートのようなポリメタクリル酸エステルなどのラテックス類も使用できる。

本発明で用いるロイコ染料としては、慣用のトリフェニルメタン系、フルオラン系、フェノチン系、オーラミン系、スピロピラン系のものが好ましい。尚、本発明のロイコ染料の例として

—6—ジエチルアミノフラリド
3,3—ビス(4—ジメチルアミ
—6—クロムフラリド
3,3—ビス(4—ジブチルアミ
フラリド
3—シクロヘキシルアミノ—6—
ラン
8—(N,N—ジエチルアミノ)—
—7—(N,N—ジベンジルアミ
ン
3—ジメチルアミノ—5,7—ジ
ラン
3—ジエチルアミノ—4—メチル

アミノ)-6-ジエチルアミノフルオラン
 2-(3,6-ビス(ジエチルアミノ)-9-(
 (4-クロルアニリノ)キサンチル)安息香酸
 ラクタム
 3-ジエチルアミノ-7-(4-クロルアニリ
 ノ)フルオラン
 3-ジブチルアミノ-7-(4-クロルアニリ
 ノ)フルオラン
 3-N-メチル-N-アミルアミノ-6-メチ
 ル-7-アニリノフルオラン
 3-N-メチル-N-シクロヘキシルアミノ-
 6-メチル-7-アニリノフルオラン
 3-(2'-ヒドロキシ-4'-ジメチルアミノ
 フェニル)-3-(2'-メトキシ-5'-クロ
 ルフェニル)フタリド
 3-(2'-ヒドロキシ-4'-ジメチルアミノ
 フェニル)-3-(2'-メトキシ-5'-ニトロ
 フェニル)フタリド
 3-(2'-ヒドロキシ-4'-ジエチルアミノフ
 エニル)-3-(2'-メトキシ-5'-メチルフ

エニル)フタリド

3-(2'-メトキシ-4'-ジメ
 エル)-3-(2'-ヒドロキシ
 5'-メチルフェニル)フタリド

この発色主剤は、視面寄りの層
 の感熱発色層)としては青、赤、
 染料ロイコ体の使用が好ましい。
 りの感熱発色層(下位の感熱発色
 色主剤としては、前記上位の感熱
 染料と組合わされた場合に黒色に
 弱に発色できるロイコ染料又は、
 発色層とは異なる色調に発色で
 あればいずれも使用できる。

また、本発明で用いる顔色剤、
 イコ染料に対して加熱時に反応
 せる種々の電子受容性物質が適
 例を示すと、次のようなフェノ
 酸性物質、有機酸性物質あるいは
 が挙げられる。
 フェノール性物質；

3,5-キシレノール、チモール、p-terti-
 ブチルフェノール、4-ヒドロキシフェノキシド、
 メチル-4-ヒドロキシベンゾエート、4-ヒド
 ロキシアセトフェノン、p-ナフトール、p-ナ
 フトール、カテコール、レゾルシン、ヒドロキノ
 ン、4-tert-オクチルカテコール、4,4-dio-
 -ブチリデンフェノール、2,2'-ジヒドロキン
 ジフェニル、2,2'-メチレンビス(4-メチル
 -6-tert-ブチルフェノール)、2,2'-ビス
 (4-ヒドロキシフェニル)プロパン、4,4-
 -イソプロピリデン-ビス(2-tert-ブチルフェ
 ノール)、4,4-dio-ブチリデンジフェノー
 ル、ピコガロール、フロログルシン、フロログル

ロキシフェノール)等。

酸性物質又はその塩。

安息香酸、没食子酸、サリチ
 酸、1-ヒドロキシ-2-ナ
 ドロキシ安息香酸、m-ヒドロ
 -ヒドロキシ安息香酸ベンジル、
 ロートルイル酸、酒石酸、蔞酸、
 エン酸、コハク酸、ステアリン
 酸、フタル酸、ホウ酸等。

感熱発色層を形成するにはこ
 の顔色剤の他に結晶剤が用いられ
 く公知のものが使用できるが具
 ニルアルコール、メトキシカル

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ル酸エステル、ポリブタジエンメタクリレートのようなポリメタクリル酸エステルなどのラテックス類も使用できる。

感熱発色層中には更に、シリカ、マグネシア、タルク、炭酸カルシウム、硫酸バリウム、果てはホルマリン樹脂、スチレン樹脂などの微粉末を添加するとともに、発色画像の鮮明度を向上させることが望ましい。また、感熱発色層を支持体上に又は下位の感熱発色層上に塗布形成するに際し、感熱発色層形成液に消泡剤、湿润剤（界面活性剤）、ワックス類、軟化点調整剤などを添加して、施工性及び粘着性を向上させることができる。

本発明の多色感熱記録材料をつくるには、染料、顔料を別々に溶解剤やその他の添加剤とともにボールミル、アトライター、サンドミル等の分散機によつて微細な粒子に粉砕分散した後これらを混合して感熱発色層形成液を調製し、これをもつて支持体上に複数層の感熱発色層を形成すればよい。かくして得られた、多色感熱記録材料によれば本発明の目的が十分達成される。

パラ安息香酸ベンジルエステル 120 g
5%ヒドロキシエチルセルロース水溶液 120 g
水 350 g
からなる混合物をアトライターで3時間粉砕してD液を調製した。

(D液)

ビスフエノールA 120 g
5%ヒドロキシエチルセルロース水溶液 120 g
水 350 g
からなる混合物をアトライターで3時間粉砕してD液を調製した。

(D液)

$\text{OH}_2(\text{OH})_2)_2 - \text{NH} - \text{CO} - \langle \bigcirc \rangle$ 80 g

次に実施例及び比較例により示す。

なお、実施例及び比較例で用いた組成を示す。

(A液)

2-〔4-〔8'-トリフルオロメチル〕アミノ〕-6-ジエチルアミノ、
(熱色発色染料)

5%ヒドロキシエチルセルロース水溶液
水

からなる混合物を磁棒ボールミルでA液を調製した。

(B液)

8-ジエチルアミノベンゾ[*a*]フルオレン、
(熱色発色染料)

5%ヒドロキシエチルセルロース水溶液
水

からなる混合物を磁棒ボールミルでB液を調製した。

(C液)

水
からなる混合物をアトライターでC液を調製した。

実施例 1

上記のA液20g、B液80g、
水溶液20g及び水30gとを1
層目の感熱発色層形成液をつく
液（基準坪量53g/m²）上に塗
布し、乾燥して約5.5g/m²の第
形成した。

この第一感熱発色層上に3%メ
水溶液をワイヤーバーで塗布し乾
g/m²の中間層を形成した。

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うに表面処理した。

実施例 2

実施例 1 で示した第 1 の発色層を形成した後、この第 1 の発色層上に実施例 1 と同様の中間層形成液を乾燥後 2.5 g/m^2 になるようワイヤーバーにて塗布し、中間層を形成した。

中間層を形成後、前記 B 液 20 g 、D 液 80 g 、F 液 40 g と 8.0 多酸化銀粉溶液 30 g と水 30 g を混合攪拌し最上層の感熱発色層形成液をつくり、中間層上にワイヤーバーにて乾燥後、 1.7 g/m^2 になるよう塗布し最上発色層を形成し 2 色感熱記録材料を作成した。続いてこれをキヤレンダーがけして平滑度がベック平滑度 $600 \sim 800$ 秒となるように表面処理した。

実施例 3

前記の A 液 20 g 、B 液 80 g と 2.0 多酸化銀粉水溶液 20 g 及び水 30 g とを混合攪拌し、第一層目の感熱発色層形成液をつくり、実施例 1 と同様の方法で乾燥後 4.5 g/m^2 の第一感熱発色層を形成したこの第一の発色層上に実施例 1 と同様の

の中間層形成液を同様の方法に
になるよう塗布し、中間層を形
中間層形成後、前記 B 液 20
F 液 40 g 、 2.0 多酸化銀粉溶
液 g を混合攪拌し、中間層上に実
法にて乾燥後 1.7 g/m^2 になる
発色層を形成し 2 色感熱記録材
いてこれをキヤレンダーがけし
平滑度 $600 \sim 800$ 秒となるよ
比較例 1

実施例 1 において、中間層を
同様にして製品を得た。

前記で得た各製品の保存性
いて試験した。この保存性試験
乾燥雰囲気中に 24 時間放置し
び 40°C で相対湿度 90% RH
24 時間放置した後の地肌濃度
X 濃度計 ND514 (グリーンフ
より測定することにより行つた
1 に示す。また、この表-1 に

初期地肌濃度の測定結果も合わせて示す。

表 - 1

	初期地肌 濃度	60°C 、乾燥 24 時間後	40°C 、 90% RH 24 時間後
実施例 1	0.09	0.16	0.14
2	0.10	0.19	0.15
3	0.09	0.14	0.11
比較例 1	0.15	0.36	0.27

表-1 から、本発明品は地肌カブリの問題がなく、すぐれた保存性を有することがわかる。

次に、前記の各製品に、厚膜抵抗型の熱ペンを

表 - 2

ペン スピード	1.6 ^{mm} / _{sec}	10 ^{mm} / _{sec}	50 ^{mm} / _{sec}
サンプル			
実施例 1	△	○	○
2	○	○	○
3	△	○	○
比較例 1	X (黒色画像に じみが生じ、赤色画 像に混色が 認められた)	△	○

○ …… 良好 △ …… 普通

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(19) Japan Patent Office (JP) (11) Kokai Publication No.
(12) Unexamined Patent Application Publication (Kokai) (A) S59-1294
(51) Int. Cl. ³ Identification Code JPO File No. (43) Kokai Publication Date: January 6, 1984
B 41 M 5/18 1 0 1 6906-2H

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Request for examination: Not requested

(5 pages in all)

(54) Title of invention: Multicolor thermosensitive recording material

(21) Patent application: S57-111070

(22) Application filing date: June 28, 1982

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Specifications

1. Title of invention

Multicolor thermosensitive recording material

2. Claims

(1) A multicolor thermosensitive recording material wherein an intermediate layer of water-soluble resin is interposed between a first thermosensitive coloring layer and a second thermosensitive coloring layer having leuco dye and developer as their main components.

3. Detailed description of the invention

The present invention concerns multicolor thermosensitive recording materials, particularly multicolor thermosensitive recording materials in which multiple thermosensitive coloring layers, which are colored in different colors according to heating temperature, are laminated.

Thermosensitive recording materials are materials wherein thermosensitive coloring layers capable of forming colored images through heating are arranged on a support medium such as paper. Thermal printers and the like that are provided with thermal heads for such heating are in wide use. Among conventional thermosensitive recording materials of this sort, those that contain colorless or lightly colored leuco dye having a lactone ring, lactam ring, spiropyran ring, or the like, as well as developer (auxiliary coloring agent), in thermosensitive coloring layers are often used, because the colors are sharp, with little fogging.

Use of thermosensitive recording materials is not limited to copying of drawing, documents, and the like, wherein colored images are easily obtained; they are also utilized in such fields as the recording of output of various information and measurement devices, including electronic computers, facsimile machines, and telex machines. Depending on the purpose of recording, however, it may of course be preferable if there is a capability of recording some part in a color

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other than that of the color of another part (display colors), especially in order to show data and numerical values more clearly.

A great deal of research and development is constantly underway in line with this aim, and hence several multicolor thermosensitive recording materials have been proposed.

When multicolor thermosensitive recording materials reported so far are examined, however, there is a problem with color separation that, for example, causes color mixture and staining in the coloring obtained in a multicolor thermosensitive coloring layer formed of a single layer coat. There are also problems with conventional multicolor thermosensitive coloring layers formed of laminated coats of two or more layers, of which the upper layer contains a substance that melts to develop color at a low temperature, and the lower layer contains a substance that melts to develop color at a high temperature, since for that reason there is a constraint as to melting point of the thermosensitive recording materials, and hence these materials are limited; and since water-soluble resin is used in the upper and lower layers in multiple-layer coating, so that part of the lower layer is dissolved when the upper layer is applied, and thus mixed with the upper layer, background fogging occurs. Arranging an intermediate layer, containing a polymer that is soluble in a non-polar solvent, between the upper and lower layers has also been proposed. However, it is difficult, in practice, to form a uniform thermosensitive coloring layer, since moistening of the intermediate layer by the coating liquid [lit., "moistening of the coating liquid and intermediate layer"] is poor when the upper layer of a water dispersion system is formed over the intermediate layer, and as a result, only unclear multicolor images are obtained.

The object of the present invention is to solve the above-mentioned prior art problems, and thereby provide a multicolor thermosensitive recording material that will make it possible to obtain high-quality multicolor images.

That is, the present invention provides a multicolor thermosensitive recording material wherein, in a multicolor thermosensitive recording material in which multiple thermosensitive coloring layers, each having leuco dye and developer for it as its main components, are laminated onto a support medium, an intermediate layer of water-soluble resin is interposed between the first thermosensitive coloring layer and the second thermosensitive coloring layer.

In the present invention, the upper layer (the second thermosensitive coloring layer) is unaffected by the lower layer (the first thermosensitive coloring layer), since a special intermediate layer is provided. There is little background fogging, and coating is satisfactory when the upper layer is arranged over the intermediate layer. In addition, coloring material that has an optional melting point can be used in the upper layer [probable typo in the Japanese: lit. "in the upper layer and coloring material that has an optional melting point can be used in the upper layer"], by adjusting the coating weight (layer thickness) of the intermediate layer. For example, when high-speed printing is preferred, and avoidance of initial background fogging and background fogging during storage are strongly preferred, a material with a high melting point can be used in the upper layer, and a material with a low melting point can be used in the lower layer. In such a case, an intermediate layer coating weight of 0.5-7 g/m² is ordinarily appropriate, with 1-5 g/m² preferred.

In the present invention, a water-soluble resin is arranged between the upper and low thermosensitive recording layers. Polyvinyl alcohol, methoxy cellulose, hydroxy cellulose, carboxy methylcellulose, carboxy ethyl cellulose, polyvinyl pyrrolidone, polyacrylamide, polyacrylic acid, starch, gelatin, or the like can be used as the water-soluble resin. Types of latex, for example styrene-butadiene copolymer, vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyacrylate ester, and polymethacrylate esters such as polybutyl methacrylate may also be used in

combination with these water-soluble resins.

Commonly used triphenylmethane dyes, fluorane dyes, phenothiazine dyes, auramine dyes, and spiropyran dyes are preferred for as leuco dyes used in the present invention. Specific examples of these leuco dyes are as follows.

3,3-bis (p-dimethylaminophenyl)-phthalide
 3,3-bis (p-dimethylaminophenyl)-6-dimethylamino phthalide (also known as crystal violet lactone)
 3,3-bis (p-dimethylaminophenyl)-6-diethylamino phthalide
 3,3-bis (p-dimethylaminophenyl)-6-chlorophthalide
 3,3-bis (p-dimethylaminophenyl) phthalide
 3-cyclohexylamino-6-chloro fluorane
 3-(N,N-diethylamino)-5-methyl-7-(N,N-dibenzylamino) fluorane
 3-dimethylamino-5,7-dimethyl fluorane
 3-diethylamino-7-methyl fluorane
 3-diethylamino-7,8-benzofluorane
 3-diethylamino-6-methyl-7-chlorofluorane
 3-pyrrolidine-6-methyl-7-anilino fluorane
 2-(N-(3'-trifluoromethylphenyl) amino)-6-diethylamino fluorane
 2-(3,6-bis (diethylamino)-9-(o-chloroanilino) xanthyl) lactam benzoate
 3-diethylamino-7-(o-chloroanilino) fluorane
 3-dibutylamino-7-(o-chloroanilino) fluorane
 3-N-methyl-N-amylamino-6-methyl-7-anilino fluorane
 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilino fluorane
 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-chlorophenyl) phthalide
 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-nitrophenyl) phthalide
 3-(2'-hydroxy-4'-diethylaminophenyl)-3-(2'-methoxy-5'-methylphenyl) phthalide
 3-(2'-methoxy-4'-dimethylaminophenyl)-3-(2'-hydroxy-4'-chloro-5'-methylphenyl) phthalide

Use of leuco dyes as the principal coloring agents is preferred for coloring blue, red, green, and so on in the thermosensitive coloring layer below the surface (upper thermosensitive coloring layer). Any leuco dye can be used as the principal coloring agent in the thermosensitive coloring layer above the support medium (lower thermosensitive coloring layer), provided that, when combined with the leuco dye in the upper thermosensitive coloring layer, it is capable of coloring in a color tone that is black or nearly black, or else is capable of coloring in a color tone that is different from that of the upper thermosensitive coloring layer.

Various electron acceptors that develop color by reacting with the aforementioned leuco dyes when heated can be used as developers in the present invention. Specific examples are phenolic substances, and of non-organic or organic acids, or salts thereof, are listed below.

Phenolic substances:

3,5-xlenol, thymol, p-tert-butylphenol, 4-hydroxyphenoxide, methyl-4-hydroxybenzoate, 4-hydroxyacetophenone, alpha-naphthol, beta-naphthol, catechol, resorcinol, hydroquinone, 4-tert-octylcatechol, 4,4-sec-butylidenephénol, 2,2'-dihydroxydiphenyl, 2,2'-methylenebis (4-methyl-6-tert-butylphenol), 2,2-bis (4-hydroxyphenol) propane, 4,4-isopropylidene-bis (2-tert-butylphenol), 4,4-sec-butylidenediphenol, pyrogallol, phloroglucinol, phloroglucinol carboxylic acid, 4-tert-octylphenol, 4-phenylphenol, 2,2-bis (p-hydroxyphenyl) butane, 4,4'-cyclohexylidene diphenyl, 2,2-bis (2,5-dibromo-4-hydroxyphenol) propane,

4,4'-isopropylidenebis (2-tert-butylphenol), 2,2'-methylenebis (4-chlorophenol), and the like.

Acids or salts thereof:

Benzoic acid, gallic acid, salicylic acid, zinc salicylate, 1-hydroxy-2-naphthoic acid, o-hydroxy benzoic acid, m-hydroxy benzoic acid, benzyl p-hydroxy benzoate, 2-hydroxy-p-toluic acid, tartaric acid, oxalic acid, maleic acid, citric acid, succinic acid, stearic acid, 4-oxydipthalic acid, boric acid, and the like.

In addition to these leuco dyes and developers, a binding agent is also used in the formation of thermoplastic coloring layers. Well-known binding agents may be used. Specific examples are: polyvinyl alcohol, methoxy cellulose, hydroxy cellulose, carboxymethyl cellulose, carboxyethyl cellulose, polyvinyl pyrrolidone, polyacrylamide, starch, gelatin, and the like.

Types of latex, for example styrene-butadiene copolymer, vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyacrylate ester, and polymethacrylate esters such as polybutyl methacrylate may also be used in combination with these water-soluble resins.

Improvement of color definition by also adding silica, magnesia, talc, calcium carbonate, barium sulfate, urea-formalin resin, styrene resin, or the like to thermosensitive coloring layers as a fine powder is preferred. Coating and thermal responsiveness can also be improved by adding antifoaming agent, wetting agent (surfactant), wax, softening point adjusting agent, or the like to the thermosensitive coloring layer forming liquid when applying and forming a thermal coloring layer over the support medium or over a lower thermal coloring layer.

In order to manufacture multicolor thermosensitive recording material of the present invention, leuco dye and developer are separately crushed into fine particles and dispersed by means of a disperser such as a ball mill, attritor, or sand mill, together with binding agent and other additives. They are then mixed to prepare a thermosensitive coloring layer forming liquid, and the mixture may be used to form multiple thermosensitive coloring layers over the support medium. The multicolor thermosensitive recording material obtained thereby sufficiently achieves the object of the present invention.

In the following, the present invention will be described in more detail, using working examples and comparative examples.

The compositions of Liquids A-F, which are used in the working examples and comparative examples, are as follows.

Liquid A

Liquid A is prepared by pulverizing a mixture comprising 150 g of 2-(N-(3'-trifluoromethylphenyl) amino)-6-diethylamino fluorane (black coloring dye), 150 g of a 5% aqueous solution of hydroxyethyl cellulose, and 450 g of water in a magnetic ball mill for 24 hours.

Liquid B

Liquid B is prepared by pulverizing a mixture comprising 150 g of 3-diethylamino benzo (a) fluorane (red coloring dye), 150 g of a 5% aqueous solution of hydroxyethyl cellulose, and 450 g of water in a magnetic ball mill for 24 hours.

Liquid C

Liquid C prepared by pulverizing a mixture comprising 120 g of benzyl parabenzoic acid ester, 120 g of a 5% aqueous solution of hydroxyethyl cellulose, and 360 g of water in an attritor for 3 hours.

Liquid D

Liquid D prepared by pulverizing a mixture comprising 120 g of bisphenol A, 120 g of a 5% aqueous solution of hydroxyethyl cellulose, and 360 g of water in an attritor for 3 hours.

Liquid E

Liquid E prepared by pulverizing a mixture comprising 80 g of $\text{CH}_3(\text{CH}_2)_{17}\text{NH-GO-}$ [benzene ring], 80 g of a 5% aqueous solution of methyl cellulose, and 240 g of water in an attritor for 3 hours.

Liquid F

Liquid F prepared by pulverizing a mixture comprising 80 g of stearylamine monoterphthalate, 80 g of a 5% aqueous solution of methyl cellulose, and 240 g of water in an attritor for 3 hours.

Working Example 1

To make the thermosensitive coloring layer forming liquid for the first layer, 20 g of the above-mentioned Liquid A, 80 g of Liquid D, 20 g of a 20% aqueous solution of oxidized starch, and 30 g of water were stirred to combine them. This was applied over high-quality paper (standard basic weight, 53 g/m²), using a wire bar, and dried to form a first thermosensitive coloring layer of approximately 5.5 g/m².

A 5% aqueous solution of methylcellulose was applied over this first thermosensitive coloring layer, using a wire brush, and dried to form an intermediate layer of approximately 1.5 g/m².

After the intermediate layer had been formed, 20 g of the above-mentioned Liquid B, 80 g of Liquid C, 20 g of an aqueous solution of oxidized starch, and 30 g of water were stirred to combine them, to make the thermosensitive coloring layer forming liquid for the uppermost layer. This was applied over the intermediate layer, using a wire bar, and dried to form an uppermost coloring layer of approximately 2.0 g/m², thus producing a two-color thermosensitive recording material. This was then surface treated, using a calendar, so that a Beck smoothness of 600-800 seconds was achieved.

Working Example 2

After the first coloring layer was formed as in Working Example 1, an intermediate layer that was 2.5 g/m² after it dried was formed over this first coloring layer by applying the same intermediate layer forming liquid as in Working Example 1 with a wire bar.

After the intermediate layer had been formed, 20 g of the above-mentioned Liquid B, 80 g of Liquid D, 40 g of Liquid E, 30 g of a 20% aqueous solution of oxidized starch, and 30 g of water were stirred to combine them, to make the thermosensitive coloring layer forming liquid for the uppermost layer. This was applied over the intermediate layer, using a wire bar, to form an uppermost coloring layer that was 1.7 g/m² after it dried, thus producing a two-color thermosensitive recording material. This was then surface treated, using a calendar, so that a Beck smoothness of 600-800 seconds was achieved.

Working Example 3

To make the thermosensitive coloring layer forming liquid for the first layer, 20 g of the above-mentioned Liquid A, 80 g of Liquid C, 20 g of a 20% aqueous solution of oxidized starch, and 30 g of water were stirred to combine them. A first coloring layer that was 4.5 g/m² after drying was formed by the same procedure as in Working Example 1. An intermediate layer that was 4.2

g/m² after drying was formed by applying the same intermediate layer forming liquid as in Working Example 1, according to the same procedure.

After the intermediate layer had been formed, 20 g of the above-mentioned Liquid B, 80 g of Liquid D, 40 g of Liquid F, 30 g of a 20% aqueous solution of oxidized starch, and 30 g of water were stirred to combine them, and spread over the intermediate layer by the same procedure as in Working Example 1, to form an uppermost coloring layer of 1.7 g/m² after drying, thus producing a two-color thermosensitive recording material. This was then surface treated, using a calendar, so that a Beck smoothness of 600-800 seconds was achieved.

Comparative Example 1

A product was obtained in the same way as in Working Example 1, except that an intermediate layer was not formed.

Tests were conducted concerning shelf life (background fogging) of each of the products obtained as described above. The shelf life tests were conducted by measuring background optical density with a Macbeth densitometer RD514 (using a green filter) after leaving the product in dry surroundings at 60° C for 24 hours, and after leaving it in surroundings with a relative humidity of 90% at 40° C for 24 hours. The results are shown in Table 1. Table 1 also shows the results of measurements of initial background optical density prior to product tests.

Table 1

	Initial background optical density	After 24 hours at 60° C, under dry conditions	After 24 hours at 40° C, 90% RH
Working Example 1	0.09	0.16	0.14
Working Example 2	0.10	0.19	0.15
Working Example 3	0.09	0.14	0.11
Comparative Example 1	0.15	0.36	0.27

From Table 1 it can be seen that the products of the present invention have superior shelf life, with no background fogging.

Two-color separation was then examined by recording delta waves with an amplitude of 40 mm, using a two-color coder having a thick film resistor type of heat stylus (two-color servocoder, manufactured by Watanabe Sokal KK). The results are shown in Table 2.

Table 2

Pen speed	1.6 mm/sec	10 mm/sec	50 mm/sec	200 mm/sec	500 mm/sec
Sample					
Working Example 1	△	○	○	○	△
Working Example 2	○	○	○	○	△
Working Example 3	△	○	○	○	○
Comparative Example 1	×	△	○	△	△
	(There was staining of black images, and color mixtures were observed in red images.)				

○: good △: ordinary ×: unsatisfactory

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⑱ 2色感熱記録方法

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明 細 書

1. 発明の名称

2色感熱記録方法

2. 特許請求の範囲

- (1) 支持体上に高温で発色する高温感熱発色層及び低温で感熱発色層とは異なる色調に発色し得る低温感熱発色層を積層した感熱記録材料が、高温感熱発色層よりも支持体に対して上層側に配置するように積層した感熱記録材料に対して、その上層側表面から2種の異なる温度で熱走査して該面及び低温感熱発色層を発色せしめることにより2種の異なる色調の発色画像を記録

【技術分野】

本発明は2色感熱記録方法に関し、更には、それぞれ異なる温度で異なる色調に2種の感熱発色層を設けた感熱記録材料の画像記録を行う方法に関するものである

【従来技術】

従来、2種の色調の画像記録を得る方は、支持体上にそれぞれ低温側及び高温側の2種の感熱及び感熱発色層を前側に位置させて積層した感熱記録材料に、層側から2種の異なる温度で熱印字を行って上層側の低温感熱発色層の発色面

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め、低温感熱発色層の発色剤としては明るい色調を生ずるものを使用せざるを得なかった。更に、2色の中の一つは、混色であるため、例えば青と赤という組合せは不可能であつた。

【目 的】

本発明は、上記した従来法の欠点を克服した2色感熱記録媒の提供を目的とし、特に、混みや混色がない鮮明なしかも任意の異なる色調の組合せによる2色の発色画像を記録させる方法を提供することを目的とする。

【構 成】

本発明によれば、支持体上に高温で発色する高温感熱発色層及び低温で該高温感熱発色層とは異なる色調に発色し得る低温感熱発色層を該高温感熱発色層が該低温感熱発色層よりも支持体に対して上層側に位置するよう積層した感熱記録材料に対して、その上層側表面から2種の異なる温度で熱走査して該低温及び該高温感熱発色層を発色せしめることにより2種の異なる色調の発色画像を記録させるにあたり、該高温感熱発色層は発色するが該低温感熱発色層が実質的に発色する温度に達

で測定した場合0.5になる場合の T_H 及び T_L の温度差を言う。

本発明においては、上記した構成の感熱記録材料を上層側表面から熱走査して発色画像を記録させるが、この場合、高温発色層の加熱発色は、高温発色層は温度 T_H 以上の温度に達するには十分であるが低温発色層が実質的に発色する温度に達するには不十分な温度及び時間で行われる。又、低温発色層の加熱発色は、高温発色層は実質的に発色しないが T_L 以上の温度で且つ低温発色層が T_L 以上の温度に達するに十分な温度で行われる。

このように加熱温度及び時間を制御することによ

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するに不十分な温度及び時間で該高温感熱発色層を加熱発色させ、該高温感熱発色層が発色しないが該低温感熱発色層が発色するに十分な温度及び時間で該低温感熱発色層を加熱発色させることを特徴とする2色法が提供される。

本発明で用いる感熱記録材料は、低温及び高温感熱発色層（以下、単に低温発色層と称す）をその間に積層するが、低温発色層と支持体の間、低温発色層の間、及び又は高温発色層の上及び、保護層、フンダーコート層等ことを妨げるものではない。

高温発色層は温度 T_H 以上で所定強度に発色するものであつて、一方低温 T_L よりも低い温度 T_L 以上の温度で以上の強度の高温発色層とは異なるものである。本発明の目的を達成する意味で、 T_H と T_L の温度差が20℃で以上あることが好ましい。尚、これは、前記所定強度がマクベスD50-

発色する発色剤を用いて熱走査を行なう発色層への加熱時間及び通電時間を制御する主成分として、下記に示すような染料と発色剤を用いた場合には、低発色する加熱時間即ち通電時間を、高発色するそれの2倍以上とすると良い。この発色における通電時間は0.5〜3ミリ秒における通電時間は2〜8ミリ秒の範囲である。

本発明に用いられる感熱記録材料は特に制限はないが、感熱発色層

の具体例としては、例えば、以下に示すようなものが挙げられる。

3,3-ビス(p-ジメチルアミノフェニル)フタリド。

3,3-ビス(p-ジメチルアミノフェニル)-5-ジメチルアミノフタリド(別名クリスタルバイオレットラクトン)。

3,3-ビス(p-ジメチルアミノフェニル)-6-ジエチルアミノフタリド。

3,3-ビス(p-ジメチルアミノフェニル)-6-クロルフタリド。

3,3-ビス(o-ジブチルアミノフェニル)フタリド。

3-シクロヘキシルアミノ-8-クロルフルオラン。

3-ジメチルアミノ-5,7-ジメチルフルオラン。

3-ジエチルアミノ-7-クロルフルオラン。

3-ジエチルアミノ-7-メチルフルオラン。

3-ジエチルアミノ-7,8-ベンズフルオラン。

3-ジエチルアミノ-8-メチル-7-クロルフルオラン。

4-ジベンジルアミノ)フルオラン。

ベンゾイルロイコメチレンブルー。

8'-クロロ-8'-メトキシ-ベンゾインドリノ-ピリロスピラン。

8'-プロモ-8'-メトキシ-ベンゾインドリノ-ピリロスピラン。

3-(2'-ヒドロキシ-4'-ジメチルアミノフェニル)-3-(2'-メトキシ-5'-クロルフェニル)フタリド。

3-(2'-ヒドロキシ-4'-ジメチルアミノフェニル)-3-(3'-メトキシ-6'-ニトロフェニル)フタリド。

3-(2'-ヒドロキシ-4'-ジメチルアミノフェニル)-3-(3'-メトキシ-6'-ニトロフェニル)フタリド。

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3-(4-ポートリル-4-エチルアミノチル-7-アニリノフルオラン。

3-ピロリジノ-6-メチル-7-アニオラン。

2-(4-(5'-トリフルオルメチルアミノ)-5-ジエチルアミノフルオラン。

2-(3,5-ビス(ジエチルアミノ)-4-ホルブアニリノ)キサンチル安臥香酸ラク

3-ジエチルアミノ-8-メチル-7-クロロメチルアニリノ)フルオラン。

3-ジエチルアミノ-7-(6-クロルフルオラン。

3-ジブチルアミノ-7-(6-クロルフルオラン。

3-N-メチル-4-アミルアミノ-6-7-アニリノフルオラン。

3-N-メチル-8-シクロヘキシルアミル-7-アニリノフルオラン。

3-ジエチルアミノ-6-メチル-7-フルオラン。

3-(4,4'-ジエチルアミノ)-5-メチル

フルオラン。

3-ジエチルアミノ-5-クロロ-7-(4-ジブチルトリフルオルメチルアニリノ)フル

3-ピロリジノ-7-(3-パークロルアミルアミノフルオラン。

3-ジエチルアミノ-5-クロル-7-(4-ニルエチルアミノ)フルオラン。

3-(4-エチル-ポートリル)-7-(4-エニルエチルアミノ)フルオラン。

3-ジエチルアミノ-7-(6-メトキシルフェニルアミノ)フルオラン。

3-ジエチルアミノ-8-メチル-7-(4

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また、本発明においては、前記ロイ
酸色剤と共に、必要に応じて、更に、こ
記材料特に慣用される増粘添加成分、
料、界面活性剤、難燃性物質又又は：
固材として用い得る。この増粘剤、増粘

アミンとの縮合物、安息香酸フェニルエステル、高級直鎖グリコール、3,4-エポキシヘキサヒドロフタル酸ジアルキル、高級ケトン、その他の能可融性有機化合物等の50~200℃の程度の融点を持つものが挙げられる。

【効 果】

上層に高温発色層、下層に低温発色層を設けた感熱記録材料を加熱温度及び時間を制御して熱走査することにより、高温加熱においては高温発色層のみが、又、低温加熱においては低温発色層のみがそれぞれ発色するので、配色による滑みのない2色画像が得られる。

【実施例】

本発明を次に実施例により更に詳細に説明する。なお、以下で部及び%は重量基準である。

実施例1

下記組成の混合液をボールミルで分散し、A、B、C、D、E及びF液を得た。なお、分散は、A及びB液は平均粒径が3μ以下、その他の液は5μ以下となるようにして行った。

A液：

ポリビニルアルコール10%水溶液 25部
水 150部

B液：

ステアリン酸アミド 10部
ポリビニルアルコール10%水溶液 10部
水 30部

以上のようにして得たA液10部、B液50部、C液20部、D液15部及び水15部を混合し、低温発色層形成用顔料液を厚さ52g/m²の上質紙上に塗布付着量が4g/m²となるように塗布乾燥して下層を形成した。このものは、市販の熱価試験機を用いて印字したところ85℃で赤色の画像（マクベス

特開59-19482

3-ジエチルアミノ-7-クロロ

フルオラン

ポリビニルアルコール10%水溶液
水

B液：

3-(8-メチル-8-シクロヘキサン
アミノ)-5-メチル-7-アニソ
フルオラン

ポリビニルアルコール10%水溶液
水

C液：

4-ヒドロキシジフェニルスルホン
ポリビニルアルコール10%水溶液
水

D液：

p-ヒドロキシ安息香酸ベンジル
ポリビニルアルコール10%水溶液
水

E液：

異素ホルマリン樹脂粉末
ステアリン酸亜鉛

上に塗布乾燥して得たものには、135℃で0.1秒（ラツテン106フィルター使用）を付す画像を与えた。

上記キヤレンダー処理後の感熱記録材料で、露光ラインヘッド（松下電工（株）製）ヘッド電力0.26V、ヘッドへの通電時間6.ヘッドエネルギー1.6ミリジュール/ドット加熱、及びヘッド電力0.57V、ヘッドへの通電時間2.8ミリ秒、ヘッドエネルギー1.6ミリジュール/ドットの高温加熱条件下で印字を行い、の発色度、滑みの程度を測定した。結果を示す。

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ポリビニルアルコール10%水溶液 10%

水 30%

(ボールミルで平均粒径5 μ 以下に分散)

次に、実施例1において、B液に代えてA液を、
又、C液に代えて下記のD液を用いた以外は同様
にして得た高感色層形成用混合液を上記下層の上
に実施例1と同様に塗布乾燥し、キャレンダ
ー処理して2色感熱記録材料を得た。

D液:

ビス(2,5-ジメチル-4-ヒドロ

キシフェニル)スルフィド 10部

ポリビニルアルコール10%水溶液 10%

水 30%

(ボールミルで平均粒径5 μ 以下に分散)

なお、この高感色層形成用混合液を市販感光
紙上に下層と同様に塗布乾燥したものは、12
0℃で0.5の発色濃度(ラフアン50フィルター使用)
を持つた赤色画像を与えた。上記のようにして得
た2色感熱記録材料を実施例1と同様に2色取
像を行った。結果は表-1に示す通りである。

比較例

特開59-1

実施例1において、高感色層形成用
液に上記液上に塗布乾燥し、次に下層
高感色層形成用混合液をその上に塗布
すれば実施例1と同様に2色感熱記録
材料を得た。結果を表-1に示す。

表-1

	低感色層条件			高感色層	
	発色	濃み	色調	発色	濃み
実施例1	○	○	赤	○	○
比較例	○	○	赤	△	×

○: 発色(又は濃み)がない

△: 発色(又は濃み)が少し

×: 発色(又は濃み)が多く

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(54) Title of invention: Two-color thermosensitive recording method

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Specifications

1. Title of invention

Two-color thermosensitive recording method

2. Claims

(1) A two-color thermosensitive recording method wherein, in order to record colored images in two different colors by heat coloring at two different temperatures, using thermal scanning from the surface of a higher layer, in a high temperature and a low temperature photosensitive coloring layer of a thermosensitive recording material laminated so that said high temperature thermosensitive recording layer, which is colored at a high temperature, and said low temperature thermosensitive recording layer, which can be colored at a low temperature in a color different from that of said high temperature thermosensitive recording layer, are positioned on a support medium such that said high temperature thermosensitive recording layer is a higher layer with respect to the support medium than is said low temperature thermosensitive recording layer, said high temperature thermosensitive recording layer is colored by heating it at a temperature and for a period of time that is insufficient for the temperature of said low temperature thermosensitive recording layer to reach a temperature at which it would be substantially colored, although said high temperature thermosensitive recording layer is colored, and said low temperature thermosensitive recording layer is heated to a temperature and for a time sufficient to color said low temperature thermosensitive recording layer, although said high temperature thermosensitive recording layer is not substantially colored.

3. Detailed description of the invention

Technical field

The present invention pertains to two-color thermosensitive recording methods. More

specifically, it pertains to methods of recording images in two colors onto a thermosensitive recording material provided with two types of thermosensitive recording layers, which are each colored at a different temperature.

Prior art

A method of thermal printing onto a thermosensitive recording material in which two layers, a low temperature and a high temperature thermosensitive recording layer, which are colored by being heated to a low and to a high temperature, respectively, are laminated such that the former is positioned as the upper layer, by heating, starting with the upper layer, at two different temperatures, so that either colored images are obtained by heating the upper low temperature thermosensitive recording layer at a low temperature, or else secondary color images are obtained by heating the upper low temperature and lower high temperature thermosensitive recording layers, is known as a conventional method enabling thermosensitive recording in two colors. The images obtained by this method have the disadvantage that it is impossible to avoid coloring the low temperature photosensitive coloring layer in the periphery of the printed image, especially when printing at a high temperature, so that the images lack clear contours, as though they were blurred. If coloring is dark in the low temperature photosensitive coloring layer, the difference in color between this and secondary color images colored by heat temperature printing may not be clear, so that the coloring agent used in the low temperature photosensitive coloring layer must be one that yields a bright color, since good two-color images discrimination cannot be obtained. Since one of the two colors is a secondary [i.e., mixed] color, it is impossible to have a combination of red and blue, for example.

Object

The object of the present invention is to provide a two-color thermosensitive recording method that improves on the disadvantages of the conventional method as recited above. In particular, the object is to provide a method of recording images combining two optional, clear, different colors without blurring or mixture of colors.

Composition

The present invention provides a two-color thermosensitive recording method wherein, in order to record colored images in two different colors by heat coloring at two different temperatures, using thermal scanning from the surface of a higher layer, in a high temperature and a low temperature photosensitive coloring layer of a thermosensitive recording material laminated so that the high temperature photosensitive coloring layer, which is colored at a high temperature, and the low temperature thermosensitive recording layer, which can be colored at a low temperature in a color different from that of the high temperature thermosensitive recording layer, are positioned on a support medium such that the high temperature thermosensitive recording layer is a higher layer with respect to the support medium than is the low temperature thermosensitive recording layer, the high temperature thermosensitive recording layer is colored by heating it at a temperature and for a period of time that is not sufficient for the temperature of the low temperature thermosensitive recording layer to reach a temperature at which it would be substantially colored, although the high temperature thermosensitive recording layer is colored, and the low temperature thermosensitive recording layer is heated to a temperature and for a time sufficient to color the low temperature thermosensitive recording layer, although the high temperature thermosensitive recording layer is not substantially colored.

The thermosensitive recording material used in the present invention is one in which a low temperature and a high temperature thermosensitive coloring layer (hereinafter, simply referred to as the high temperature coloring layer and the low temperature coloring layer) are laminated onto a support medium. However, this does not prevent other layers, such as protective layers, undercoat layers, and the like from being arranged, as necessary, between the low temperature coloring layer and the support medium, between the high temperature coloring layer and the low temperature coloring layer, and or on the upper surface of the high temperature coloring layer.

The high temperature coloring layer is colored at an optical density that is \geq the predetermined optical density, at a temperature that is \geq a temperature T_H . On the other hand, the low temperature coloring layer is colored with a color that is different from that of the high temperature coloring layer, in an optical density that is \geq the above-mentioned predetermined optical density, at a temperature that is \geq a temperature T_L but lower than T_H . In order to effectively achieve the object of the present invention, the preferred temperature difference between T_H and T_L is $\geq 20^\circ \text{C}$, with $\geq 30^\circ \text{C}$ especially preferred. The temperature difference in this case is the difference in temperature between T_H and T_L when the above-mentioned predetermined optical density is 0.5, as measured using a Macbeth densitometer RD-514.

The thermosensitive recording material in the composition of the present invention as recited above is made to record colored images by thermal scanning from the surface of the upper layer. Thermal coloring of the high temperature thermosensitive recording layer is carried out by heating it at a temperature and for a period of time that is sufficient for its temperature to reach $\geq T_H$, but that is not sufficient for the temperature of the low temperature thermosensitive recording layer to reach a temperature at which it would be substantially colored. Thermal coloring of the low temperature thermosensitive recording layer is carried out for a period of time that is sufficient for its temperature to reach $\geq T_L$, although the high temperature thermosensitive recording layer is not substantially colored.

By controlling the heating temperature and time in this way, it is possible to color the upper high temperature thermosensitive recording layer only by thermal scanning at a high temperature, and to color the lower low temperature thermosensitive recording layer only by thermal scanning at a low temperature. Therefore, sharply contoured color images, free of blurring, can be obtained, since, unlike the conventional method, there is no mixing of colors as a result of coloring the upper and lower coloring layers at the same time. On the other hand, the optional colors can be combined as desired.

The above-mentioned control of temperature and time during recording is effected by controlling the printing voltage to the heating element, and the period of time it is energized, when thermal scanning is effected using a heating element that heats by energizing a thermal head, thermal pen, or the like. When using leuco dye and developer are the main components constituting the coloring system of low temperature and high temperature coloring layers, as described below, the preferred heating time, that is, energizing time, for the low temperature thermosensitive recording layer is ≥ 2 times that for the high temperature thermosensitive recording layer. Hence, an energizing time of 0.5-3 milliseconds is appropriate for the high temperature thermosensitive recording layer, and an energizing time of 2-8 milliseconds is appropriate for the low temperature thermosensitive recording layer.

There are no particular restrictions as to the coloring system of thermosensitive recording material used in the present invention, but use of leuco dye and developer is preferred from the standpoint of sensitivity and color optical density.

Leuco dyes are appropriate for use in the present invention, either singly or in combinations

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of two or more, but selection of leuco dyes that are appropriate for use in this sort of photosensitive material, for example triphenylmethane dyes, fluorane dyes, phenothiazine dyes, auramine dyes, and/or spiropyran dyes, is preferred. The following are specific examples of leuco dyes.

- 3,3-bis (p-dimethylaminophenyl)-phthalide
- 3,3-bis (p-dimethylaminophenyl)-6-dimethylamino phthalide (also known as crystal violet lactone)
- 3,3-bis (p-dimethylaminophenyl)-6-diethylamino phthalide
- 3,3-bis (p-dimethylaminophenyl)-6-chlorophthalide
- 3,3-bis (p-dimethylaminophenyl) phthalide
- 3-cyclohexylamino-6-chloro fluorane
- 3-dimethylamino-5,7-dimethyl fluorane
- 3-diethylamino-7-chlorofluorane
- 3-diethylamino-7-methyl fluorane
- 3-diethylamino-7,8-benzofluorane
- 3-diethylamino-6-methyl-7-chlorofluorane
- 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilino fluorane
- 3-pyrrolidine-6-methyl-7-anilino fluorane
- 2-(N-(3'-trifluoromethylphenyl) amino)-6-diethylamino fluorane
- 2-(3,6-bis (diethylamino)-9-(o-chloroanilino) xanthyl) lactam benzoate
- 3-diethylamino-6-methyl-7-(m-trichloromethylanilino) fluorane
- 3-diethylamino-7-(o-chloroanilino) fluorane
- 3-dibutylamino-7-(o-chloroanilino) fluorane
- 3-N-methyl-N-amylamino-6-methyl-7-anilino fluorane
- 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilino fluorane
- 3-diethylamino-6-methyl-7-anilino fluorane
- 3-(N,N-diethylamino)-5-methyl-7-(N,N-dibenzylamino) fluorane
- benzoyl leuco methylene blue
- 6'-chloro-8'-methoxy-benzo *indolyno-pyrroli-spirane* [not confirmed]
- 6'-bromo-3'-methoxy-benzo *indolyno-pyrroli-spirane* [not confirmed]
- 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-chlorophenyl) phthalide
- 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-nitrophenyl) phthalide
- 3-(2'-hydroxy-4'-diethylaminophenyl)-3-(2'-methoxy-5'-methylphenyl) phthalide
- 3-(2'-methoxy-4'-dimethylaminophenyl)-3-(2'-hydroxy-4'-chloro-5'-methylphenyl) phthalide
- 3-morpholino-7-(N-propyl-trifluoromethylanilino) fluorane
- 3-pyrrolidine-7-trifluoromethylanilino fluorane
- 3-diethylamino-5-chloro-7-(N-benzyl-trifluoromethylanilino) fluorane
- 3-pyrrolidine-7-(di-p-chlorophenyl) methylamino fluorane
- 3-diethylamino-5-chloro-7-(alpha-phenylethylanilino) fluorane
- 3-(N-ethyl-p-toluidino)-7-(alpha-phenylethylanilino) fluorane
- 3-diethylamino-7-(o-methoxycarbonylphenylamino) fluorane
- 3-diethylamino-5-chloro-7-(alpha-phenylethylanilino) fluorane
- 3-diethylamino-7-piperidino fluorane
- 2-chloro-3-(N-methyltoluidino)-7-(p-n-butylanilino) fluorane
- 3-(N-benzyl-N-cyclohexylamino)-5,6-benzo-7-alpha-naphthylamino-4'-bromo fluorane
- 3-diethylamino-6-methyl-7-*mesitydino* [not confirmed]-4'-5'-benzo fluorane

Various electron acceptors that develop color by reacting with the aforementioned leuco dyes when heated can be used as developers in the present invention. Specific examples are phenolic substances, and organic or non-organic acids, or salts thereof, as listed below.

Gallic acid, salicylic acid, 3-isopropylsalicylic acid, 3-cyclohexylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 3,5-di-alpha-methylbenzylsalicylic acid, 4,4'-isopropylidenebiphenol, 4,4'-isopropylidenebis (2-chlorophenol), 4,4'-isopropylidenebis (2,6-dibromophenol), 4,4'-isopropylidenebis (2,6-dichlorophenol), 4,4'-isopropylidenebis (2-methylphenol), 4,4'-isopropylidenebis (2,6-dimethylphenol), 4,4'-isopropylidenebis (2-tert-butylphenol), 4,4'-sec-butylidene diphenol, 4,4'-cyclohexylidenebiphenol, 4,4'-cyclohexylidenebis (2-methylphenol), 4-tert-butylphenol, 4-phenylphenol, 4-hydroxyphenoxide, alpha-naphthol, beta-naphthol, 3,5- xlenol, thymol, methyl-4-hydroxybenzoate, 4-hydroxyacetophenone, novolak phenol resin, 2,2'-thiobis (4,5-cyclophenol), catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, phloroglucinol carboxylic acid, 4-tert-octylphenol, 2,2'-methylenebis (4-chlorophenol), 2,2'-methylenebis (4-methyl-6-tert-butylphenol), 2,2'-dihydroxydiphenyl, p-hydroxy ethyl benzoate, p-hydroxy propyl benzoate, p-hydroxy butyl benzoate, p-hydroxy p-chlorobenzyl benzoate, p-hydroxy o-chlorobenzyl benzoate, p-hydroxy n-octyl benzoate, benzoic acid, zinc salicylate, 1-hydroxy-2-naphthoic acid, 2-hydroxy-6-naphthoic acid, zinc 2-hydroxy-6-naphthoate, 4-hydroxydiphenylsulfone, 4-hydroxy-4'-chlorodiphenylsulfone, bis (4-hydroxyphenyl) sulfide, 2-hydroxy-p-toluic acid, zinc 3,5-di-tert-butyl salicylate, tin 3,5-di-tert-butyl salicylate, tartaric acid, oxalic acid, maleic acid, citric acid, succinic acid, stearic acid, 4-hydroxyphthalic acid, boric acid, and the like.

Various commonly used binding agents can be appropriately employed in order to bind and support the leuco dye and developer on the support medium. For example, polyvinyl alcohol; starch and derivatives thereof; cellulose derivatives such as methoxy cellulose, hydroxyethyl cellulose, carboxy methyl cellulose, methyl cellulose, and ethyl cellulose; water soluble polymers such as sodium polyacrylate, polyvinyl pyrrolidone, amide acrylate-acrylic acid ester copolymer, amide acrylate-acrylic acid ester-methacrylic acid ternary copolymer, styrene-anhydrous maleic acid copolymer, alkali salt of isobutylene-anhydrous maleic acid copolymer, polyacrylamide, sodium alginate, gelatin, and casein; and latexes such as polyvinyl acetate, polyurethane, styrene-butadiene copolymer, polyacrylic acid, polyacrylic acid ester, vinyl chloride-vinyl acetate copolymer, polybutyl methacrylate, ethylene-vinyl acetate copolymer, and styrene-butadiene-acryl ternary copolymer may be used.

Auxiliary additive components commonly used in this type of thermal recording material, for example fillers, surfactants, thermoplastic substances (or lubricants) can also be used concomitantly with leuco dye and developer in the present invention, as necessary. In such cases, inorganic fine powders such as calcium carbonate, silica, zinc oxide, titanium oxide, aluminum hydroxide, zinc hydroxide, barium sulfate, clay, talc, and surface-treated calcium and silica, as well as organic fine powders such as urea-formalin resin, styrene-metacyclic acid copolymer, and polystyrene resin can be used as fillers. Higher fatty acids and their esters, amides and their metallic salts, various types of wax, condensation products of aromatic carboxylic acids and amines, benzoic acid phenyl esters, higher straight chain glycols, 3,4-epoxy-dialkyl hexahydrophthalate, higher ketones, and other thermoplastic organic compounds with melting points of approximately 50-200° C may be cited as examples of thermoplastic substances.

Effect

Two-color images are obtained, without blurring due to color mixing, by thermal scanning,

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with heating temperature and time controlled, on thermosensitive recording material wherein are arranged an upper high temperature coloring layer and lower low temperature coloring layer, of which only the high temperature coloring layer is colored during high temperature heating, or only the low temperature coloring layer during low temperature heating.

Working examples

The present invention will next be described in more detail, using working examples. In the following, values expressed in "parts" and "%" are based on weight.

Working Example 1

Liquids A, B, C, E, G, and H were prepared by dispersing the liquid mixtures of which they were composed in a ball mill. Dispersion was such that the mean particle size was $\leq 3 \mu$ in Liquids A and B, and $\leq 5 \mu$ in the other liquids.

Liquid A:

3-diethylamino-7-methyl fluorane	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

Liquid B:

3-(N-methyl-N-cyclohexamino)-6-methyl-7-anilino fluorane	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

Liquid C:

4-hydroxydiphenylsulfone	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

Liquid E:

p-hydroxy benzyl benzoate	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

Liquid G:

urea-formalin resin, fine powder	20 parts
zinc stearate	5 parts
polyvinyl alcohol, 10% aqueous solution	25 parts
water	150 parts

Liquid H:

amide stearate	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

10 parts of Liquid A, 60 parts of Liquid E, 20 parts of Liquid G, and 15 parts of Liquid H, obtained as shown above, were mixed with 15 parts of water, and a layer that was approximately 4

g/m² when dried was formed, adhering onto a high-quality paper surface, using 52 g/m² basic weight of this low temperature coloring layer forming liquid mixture. This layer yielded a red image (optical density according to the Macbeth densitometer RD-514 (using a Wratten 50 filter): 0.5) when printed on at 85° C, using a commercially available thermal gradient testing device. A high temperature coloring layer forming liquid mixture comprising 10 parts of Liquid B, 40 parts of Liquid C, 20 parts of Liquid G, and 30 parts of water was next applied over the low temperature coloring layer obtained as described above so as to be 3.5 g/m² after drying. This was calendar treated so that a Beck smoothness of approximately 500 seconds was achieved. When the high temperature coloring layer forming liquid mixture as recited above was exactly the same as the liquid mixture used for the low temperature coloring layer, the material obtained over the commercially available high-quality paper yielded a black image having a color optical density of 0.5 (using a Wratten 106 filter) at 135° C.

Following the calendar treatment, the thermosensitive recording material was printed on, using a thin film line head (manufactured by Matsushita Electric Works, Ltd.), with 0.26 W head electrical power, 6.2 millisecond head energizing time, and 1.6 millijoule of head energy as conditions for low temperature heating, and 0.57 W head electrical power, 2.8 millisecond head energizing time, and 1.6 millijoule of head energy as conditions for high temperature heating. At this time, the degree of color mixture and blurring was observed. The results are shown in Table 1.

Working Example 2

The lower layer was formed in the same way as in Working Example 1, except that Liquid B was used instead of Liquid A; Liquid F, with the composition shown below, was used instead of Liquid E; and water was used instead of Liquid H. A black image with a color optical density of 0.5 (using a Wratten 105 filter) was obtained at 78° C with this material.

Liquid F:

N-4'-methylphenyl-m-aminophenol	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

(Dispersed in a ball mill such that mean particle size was $\leq 5 \mu$)

Next, a two-color photosensitive recording material was obtained by applying a high temperature coloring layer forming liquid mixture, obtained in the same way as in Working Example 1, except that Liquid A was used instead of liquid B, and Liquid D, obtained as recited below, was used instead of Liquid C, drying in the same way as in Working Example 1, and calendar treating.

Liquid D:

bis (2,5-dimethyl-4-hydroxyphenyl) sulfide	10 parts
polyvinyl alcohol, 10% aqueous solution	10 parts
water	30 parts

(Dispersed in a ball mill such that mean particle size was $\leq 5 \mu$)

When this high temperature coloring layer forming liquid mixture was applied over commercially available high-quality paper in the same way as with the lower layer, a red image with a color optical density of 0.5 (using a Wratten 50 filter) was obtained at 120° C. Two-color recording was carried out on the two-color photosensitive recording material thus obtained, in the same way as in Working Example 1. The results are shown in Table 1.

Comparative Example

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A two-color photosensitive recording material was obtained in the same way as in Working Example 1, except that a high temperature coloring layer forming liquid mixture was first applied over high-quality paper, and dried, after which the low temperature coloring layer forming liquid mixture that had been used as the lower layer was applied over [the high temperature coloring layer forming liquid mixture], and dried. Two-color recording was carried out on this in the same way as in Working Example 1. The results are shown in Table 1.

Table 1

	High temperature coloring conditions			Low temperature coloring conditions		
	Color mixing	Blurring	Color	Color mixing	Blurring	Color
Working Example 1	○	○	red	○	○	black
Working Example 2	○	○	black	△	○	red
Comparative Example	○	○	red	×	×	black

○: No color mixing (or blurring)

△: A small amount of color mixing (or blurring) observed

×: A large amount of color mixing (or blurring) observed

Patent applicant: Ricoh Corporation

Patent agent: Toshiaki Ikeura, Patent Attorney

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